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Elektronenverdeling in cyaanuurzuur

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SUMMARY

Bond lengths and angles obtained from X-ray diffraction are an important source of information about the nature of the chemical bond. X-ray diffraction may, in addition, yield even more detailed information on the chemical bond because, in principle, the distribution of the valence electrons in the molecule can be deduced from the diffraction data by a Fourier synthesis. The first attempts to determine the distribution of valence electrons by X-ray methods have been made around 1939 for diamond, rock salt and hexamethylenetetramine. From these and more recent investigations it was concluded that accurate diffraction intensities and a very careful interpretation of the results are required.

It was our objective to find out, using the example of cyanuric acid, whether the recent improvements in both experimental and theoretical X-ray diffraction techniques may make it possible to test approximate wave functions by means of X-ray diffraction.

The structure of cyanuric acid was (re)determined at room temperature (Ch. 2) and at 100°K. The intensities at 100°K were measured accurately (4.3.4) on a three circle diffractometer constructed in the workshop of the chemistry department of the University of Groningen. Use was made of molybdenum radiation and balanced filters, the ω scan method was applied and a scintillation counter with pulse height discrimination was used as detector. Attenuation filters were used to reduce the errors due to non-linearity to 1%. All reflections up to $\sin \theta/\lambda = 0.8 \text{ \AA}^{-1}$ were measured. Cooling was achieved with a flow of the vapour of boiling nitrogen surrounded by a jacket of nitrogen gas of about room temperature (Ch. 3). The various checks and corrections on the measured intensities such as corrections for absorption in crystal and capillary, extinction and multiple reflection, are described in Ch. 4.

The diffraction data were first interpreted in terms of a structure model consisting of spherical atoms (Ch. 5). The coordinates and the anisotropic vibration parameters of the atomic model were altered until the best least squares agreement was obtained between calculated and observed structure factors.

Individual weights, corresponding to the accuracy of the measurements, were assigned. A Fourier map was then calculated representing the difference between the experimentally observed electron density distribution and the one corresponding to the best model constructed of spherical atoms. The difference Fourier (Fig. 6.10) showed maxima on each bond and at possible locations of the oxygen lone pairs. The least squares refinement was repeated using only lower angle diffraction data ($\sin \theta/\lambda < 0.63 \text{ \AA}^{-1}$). It appeared that the thermal parameters of the atoms of the model changed appreciably and that the maxima in the difference Fourier became less pronounced. This indicates that part of the density differences are compensated for by the thermal parameters assigned to the atoms in the least squares analysis. It is to be expected that this occurs to a smaller extent in the complete refinement based on reflections up to $\sin \theta/\lambda = 0.8 \text{ \AA}^{-1}$.

From a theoretical point of view, the electron density distribution should be compared with a model constructed not from spherical atoms but from atoms in the valence state. Therefore a refinement based on such a model was undertaken. To this end, we calculated by the method of Dawson (1964b), the scattering power of valence state atoms with a π -electron population as calculated for the molecule by the Hückel method including ω technique. After a least squares refinement based on these scattering powers a difference Fourier was calculated (Fig. 6.11). This difference map shows in the molecular plane regions of positive electron density on each bond, containing an excess of over 0.2 electron per bond; these regions were ascribed mainly to electrons in σ bonds. The excess density is somewhat larger near the nitrogen atoms than near the carbon atoms which may be due to the larger electronegativity of the nitrogen atom. The lone pair maxima near oxygen which were observed in the difference density corresponding to the model with spherical atoms (Ch. 5) have now disappeared. This proves that they are localized in sp^2 orbitals as assumed for the aspherical oxygen atoms of this new model. Out of the plane of the molecule minima are observed at about 0.7 \AA above and below the nitrogen and carbon atoms, combined with positive regions at closer distance. These maxima and minima were tentatively explained as a possible result of the delocalization of the π orbitals and from a possible contraction of the orbitals.

A comparison of the thermal parameters and coordinates after "spherical" and "aspherical" refinement respectively shows that, even when using diffraction data up to $\sin \theta/\lambda = 0.8 \text{ \AA}^{-1}$, corre-

lation errors in the (thermal) parameters remain. These errors are due to the tendency of the parameters to compensate true density differences in a least squares refinement.

Our conclusion is that modern X-ray diffraction techniques can give clear indications of bonding effects. The strong correlation combined with the lack of a good theoretical model prevented us however from pronouncing upon the quantitative electron distribution in cyanuric acid.

In 6.8 we have indicated in which way such errors may be avoided in future work. Important factors are accurate measurement of all reflections up to very high $\sin \theta/\lambda$ values at very low temperatures, determination of the absolute intensity scale, use of neutron diffraction data for determination of thermal parameters and nuclear positions and comparison of the electron density distribution with more detailed theoretical models. Whereas at present a good qualitative picture of the distribution of the valence electrons can be deduced from X-ray diffraction it is to be expected that in the future quantitative information can be obtained.